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[54] ANTISTATICALLY CONDUCTIVE MASKING FILM FOR ELECTROSTATIC SPRAY PAINTING

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[63] Continuation of Ser. No. 168,303, Mar. 15, 1988, abandoned.

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[58] Field of Search 524/910, 911, 913, 236, 524/243, 247; 428/343, 345, 922, 77, 78, 79, 195, 201, 206, 208; 260/DIG. 19, DIG. 20; 427/14.1, 282

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[57] ABSTRACT

A masking film suitable for masking during electrostatic spray painting is disclosed. In one embodiment the masking film is made from an acid copolymer/quaternary amine mixture which is permanently antistatic. The acid copolymer is a copolymer of (i) a major amount by mol % of an alpha-olefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha,beta-ethylenically unsaturated carboxylic acid. The quaternary amine is of the formula $[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$ wherein R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2; each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, trifluoroacetate, propionate, tartrate or carbonate. In a second embodiment, the masking film is made from a polyolefin containing a particulate conductive filler.

11 Claims, No Drawings

ANTISTATICALLY CONDUCTIVE MASKING FILM FOR ELECTROSTATIC SPRAY PAINTING

This is a file wrapper continuation application of application Ser. No. 168,303, filed on Mar. 15, 1988, now abandoned.

FIELD OF THE INVENTION

This invention relates to antistatically conductive masking films, which are useful to cover areas that it is desired to keep free of paint during electrostatic spray painting. Such electrostatic spray painting is also colloquially known as Ransburg painting and is commonly used for the painting of items such as parts for automobiles, trucks, refrigerators, cabinets and the like.

The films may comprise a thermoplastic polymer in admixture with an antistatic agent. For instance, the masking films may be made from an acid copolymer/quaternary amine mixture. In addition to being useful as films for masking during electrostatic spray painting, the new, acid copolymer/quaternary amine mixtures of the invention are also useful in making film for packaging for electronic devices that are sensitive to static electricity.

Alternatively, the masking film may comprise a polymeric film such as a polyolefinic film loaded with an agent that is a particulate, conductive filler, such as carbon black, aluminum, tin, nickel, zinc, copper, iron, or metallized mica. Also, if desired, the masking films may comprise the acid copolymer/quaternary amine mixture, described in the above paragraph, mixed into a polyolefinic film loaded with such a particulate conductive filler.

BACKGROUND OF THE INVENTION

High-speed production line painting requires high-volume painting equipment, typical of which is the electrostatic sprayer. This sprayer routinely delivers a high volume of liquid per unit time, in the form of electrostatically charged droplets. Paint loss may be half that of other spray processes. The charge may be delivered typically as 50,000 to 100,000 volts. Droplets are able to "go around corners" and deposit on areas otherwise inaccessible. The charge on the substrate being sprayed is opposite to that of the droplets, and the substrate is grounded so as to bleed off any built-up electrostatic charge. If this charge is not bled off, the article will build up a charge the same as that of the spray particles, and will repel further particles. If the substrate is metal, there is generally no problem in achieving an effective ground. However, many substrates are non-conducting (insulative) plastics, which are best grounded by first coating them with a conductive pre-coat, which can then be connected to a grounding system. The thus coated substrate can then be routinely electrostatically spray-painted. Various conductive precoats or primers are commercially available for this purpose.

Items must be grounded to be electrostatically spray painted. Commonly used masking materials are unsuitable for masking during such painting because they are dielectrics, i.e. insulators, and thus cannot be grounded.

Electrostatic spray painting is described in the Kirk-Othmer Encyclopedia of Chemical Technology, 3d edition, volume 6, a Wiley-Interscience Publication, at pages 414–418, particularly at pages 417 and 418.

It is well known that static charge can be reduced by increasing the moisture content of the atmosphere, and thus the approach in the past has been to use an antistatic agent which will modify the inherently dielectric polymer to impart hydrophilic properties to it by providing functional groups that attract moisture to it. For instance, it is well known to apply external antistatic agents onto polymers by conventional coating or painting methods. Also, it is well known to employ internal antistatic agents which are volume dispersed by admixing in the polymer; i.e. incorporated into the polymer by compounding or extrusion prior to or during molding or film-forming operations, and which work by migrating to the polymer surface. This migration is colloquially referred to in the art of antistatic polymer technology as a "blooming" or "bleeding" effect. When the antistatic agent has not remained volume dispersed but instead has bloomed or bled to the surface, the mechanism for moisture attraction is the same as with the painted on external antistatic agents. The atmospheric moisture is attracted causing decay or dissipation of static charges, i.e. such films depend on ambient humidity. Accordingly a high rate of blooming is required. Such films can overbloom and lose their antistatic character if subjected to a 24 hour water shower or a prolonged heat exposure.

Many patents show quaternary amines (also referred to as quaternary ammonium compounds or salts) as antistatic agents. Examples are U.S. Pat. No. 3,324,091 to Sauides, U.S. Pat. Nos. 3,445,440, and 3,517,045 both to Susi and Arthen, U.S. Pat. No. 3,894,077 to Horikawa et al, U.S. Pat. No. 4,104,175 to Martinsson et al, U.S. Pat. No. 4,268,583 and T961009 both to Hendy, and U.S. Pat. No. 4,605,684 to Pcolinsky.

Also of interest is Japanese Published Patent Application Kokai No. 59-47243, Ito et al, assignors to Mitsui (published Mar. 16, 1984) which shows an electrically conductive resin composition comprising ethylene/alpha,beta unsaturated carboxylic acid copolymer and a tertiary alkanolamine.

More particularly, U.S. Pat. No. 3,933,779 issued Jan. 20, 1976 to Baron et al assignors to Fine Organics discloses an antistatic polymer blend comprising a synthetic polymer and an antistatically effective amount of a diethoxy-methyl-C_4 to C_{18} alkyl-toluene sulfonate wherein the alkyl of 4 to 18 carbon atoms may be unsubstituted or substituted by halo or aryl. It is believed that Emerstat 6660 is a diethoxylated alkyl ammonium salt of the formula (A) $(A')N[(CH_2CH_2O)_nH]_2{}^+A'OSO_3{}^{-}$— which is further described below.

Of general interest is U.S. Pat. No. 4,678,836 (July 7, 1987) McKinney et al assignors to Dow Chemical. It shows blends of linear low density polyethylene (LLDPE) and ethylene-acrylic acid (EAA).

Also, it is noted polyolefin loaded with carbon is commercially available.

SUMMARY OF THE INVENTION

The antistatically conductive masking films of the invention will exhibit a Ransburg meter reading of about 90 or above at $35\pm5\%$ relative humidity. Under production conditions this Ransburg value may be varied by increasing or decreasing the relative humidity. The Ransburg test is further discussed below.

The masking film may be made into a single ply and/or multiple ply film, and additional advantageous features such as tougher films, further described below, may be obtained when such films are irradiated by elec-

tron beam. If desired, the film could be a heat-shrinkable or vacuum skin packaging film. Also such a film is useful to make a package for devices in a medical operating room where explosive oxygen and/or ether are present and thus protection from static electricity must be provided, or may be advantageously employed for any use requiring a plastic with a decreased tendency to accumulate dust.

In the embodiment wherein the film is made from an acid copolymer/quaternary amine mixture, the acid copolymer/quaternary amine films of the invention will dissipate an applied charge of ±5000 volts direct current (Vdc) in about 3000 milliseconds (ms) or less, more preferably about 2000 ms or less. The acid copolymer/-quaternary amine films of the invention still will exhibit this static decay time behavior after a 24 hour water shower. In the preferred embodiments, the acid copolymer/quaternary amine films also will still exhibit this static decay time behavior after 12 days in a hot (approximately 70° C.) oven. This is true even if the acid copolymer/quaternary films were not previously irradiated by electron beam. Thus, the antistatic effect is permanent and non-bleeding, without any requirement for electron beam "curing". By "permanent, non-bleeding" antistatic characteristics is meant the film exhibits a static decay time (hereinafter abbreviated as SDT) under about 3000 milliseconds (hereinafter abbreviated as ms) when the static decay test using 5000 volts direct current (hereinafter abbreviated as Vdc) is conducted as per Federal Test Method 101c, Method 4046.1, after a 24-hour water shower, i.e. the antistat property is not washed out by the shower. In the preferred embodiments, the film will also still have this SDT of about 3000 ms or less even after 12 days in a hot (approximately 70° C.) oven. Accordingly, very satisfactory acid copolymer/quaternary amine films may be obtained absent any electron beam irradiation. Thus the irradiation does not have to be employed but may be employed if desired to achieve enhanced toughness and the like as further described below. The new, acid copolymer/quaternary amine mixture may be molded or extruded alone or together with polymers known for their strength such as ethylene vinyl acetate (EVA), polypropylene (PP) or linear low density polyethylene (LLDPE), and the resultant film is useful for making packaging, such as a bag or over-wrap, for electronic devices that are sensitive to static electricity.

More particularly the acid copolymer/quaternary amine films are useful as masking for electrostatic spray painting. Alternatively, as stated above, the masking films may comprise a polymeric film such as a polyolefinic film loaded with particulate conductive filler. The masking film may be coated with adhesive.

In the electrostatic spray painting of automobiles, trucks, refrigerators, and the like, the surface to be painted is grounded, and must be electrically conductive. Many commonly used masking materials (e.g. masking tape, plastic film) are not suitable for electrostatic spray painting because they are electrical insulators and cannot be grounded. Such insulating materials can accumulate a static charge and cause paint repulsion, sparking/explosion hazards, and/or dust attraction. In the absence of a suitable masking material, the surface to be electrostatically spray painted would have to be sprayed alone and then attached to a non-painted surface. For instance a pick-up truck fender would have to be electrostatically spray painted and then assembled to a non-painted bed liner for a pick-up truck. With the present invention the antistatically conductive film can be grounded and will not cause paint repulsion. Therefore, the bed liner not to be painted and the fender to be painted can be assembled first; then the bed liner can be masked with the antistatically conductive film of the invention; and then the assembly electrostatically spray painted. Time is saved and the problem of chipping an already painted fender when assembling it to a non-painted bed liner is avoided.

Therefore, it is an object of the present invention to provide an antistatically conductive film useful as a masking during electrostatic spray painting. It is an advantage of the masking film that it will not repel paint, will not cause a sparking/explosion problem and will avoid the accumulation of dust. It is a feature of the masking film that it can be grounded.

The present invention provides an antistatically conductive film suitable for masking during electrostatic spray painting said film comprising either (1) a polymer containing carboxylic acid moieties and an anti-statically effective amount of a quaternary amine, (2) a polyolefin containing a particulate conductive filler, or (3) a mixture of (1) and (2). The present invention also provides this masking film wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alphaolefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha, beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

wherein

R^1 is selected from H, aryl, C_1 to C_{50} alkyl optionally having one or more non-contiguous C=O or NHC=O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4, is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, trifluoroacetate, citrate, propionate, tartrate or carbonate. The invention also provides for a film comprising this mixture. Preferably, C_1 to C_8 alkyl phosphate is methyl phosphate or ethyl phosphate, C_1 to C_8 alkyl sulfate is methyl sulfate or ethyl sulfate, and C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate is methanesulfonate, butanesulfonate, benzenesulfonate, or C_1 to C_{18} alkyl benzenesulfonate.

Preferably, the polyolefin is ethylene vinyl acetate, ethylene alkyl acrylate, polypropylene, low density polyethylene, medium density polyethylene, high density polyethylene, linear low density polyethylene, very low density linear polyethylene, or mixtures thereof. The loading of particulate conductive filler in the polyolefin should be at least about 0.001%, preferably at least about 0.005% by weight, said particulate filler preferably being selected from carbon, aluminum, tin, nickel, zinc, copper, iron, or metallized mica.

The present invention also provides any of the above masking films wherein the film is coated on one side with an adhesive to facilitate attachment to a substrate.

The present invention also provides a method for making an antistatically conductive film suitable for masking during electrostatic spray painting, said method comprising:

(1) mixing with heat (A) a polymer containing carboxylic acid moieties and (B) an antistatically effective amount of a quaternary amine wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alphaolefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha, beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, trifluoroacetate, propionate, tartrate or carbonate; and

(2) forming the resultant into a film having one or more layers.

The present invention also provides a permanently antistatically conductive film suitable for masking during electrostatic spray painting comprising a film obtained from mixing with heat and forming into a film (A) ethylene-acrylic acid or ethylene-methacrylic acid and (B) a quaternary amine of the formula $[R^1R^2R^3R^4N]^+[X]^-$ where R^1 is a C_4 to C_{30} straight or branched alkyl optionally including one or more ether linkages, each of R^2 and R^3 and R^4 is the same or different and selected from methyl or ethyl, and X is chloride, methyl sulfate, or ethyl sulfate.

The present invention also provides a film comprising a 5-layer, antistatically conductive film suitable for masking during electrostatic spray painting having the layers in direct surface-to-surface contact with each other in the following order:

(1) a first layer, said layer being an outside layer comprising about 90% or more by weight of ethylene vinyl acetate copolymer,

(2) a second layer, said layer being an interior layer comprising about 65% or more by weight ethylene vinyl acetate copolymer, and about 35% or less by weight of a mixture of (A) a polymer containing carboxylic acid moieties and (B) an antistatically effective amount of a quaternary amine wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alpha-olefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha,beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

wherein

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, trifluoroacetate, propionate, tartrate, or carbonate,

(3) a third layer, said layer being a core layer comprising about 65% or more by weight of a mixture of linear low density polyethylene copolymer and ethylene vinyl acetate copolymer and about 35% or less by weight of a mixture of (A) a polymer containing carboxylic acid moieties and (B) an antistatically effective amount of a quaternary amine wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alpha-olefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha,beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

wherein

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, trifluoroacetate, propionate, tartrate, or carbonate.

(4) a fourth layer, comprising an interior layer the same as layer (2); and

(5) a fifth layer, comprising an outside layer the same as layer (1).

The present invention also provides an antistatically conductive film suitable for masking during electrostatic spray painting said film comprising (A) a polymer containing carboxylic acid moieties and (B) an antistatically effective amount of a quaternary amine wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alpha-olefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha,beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

wherein

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, trifluoroacetate, propionate, tartrate, or carbonate.

The present invention also provides a method of masking an article for electrostatic spray painting comprising covering the article with an antistatically conductive film of either (1) a polymer containing carboxylic acid moieties and an antistatically effective amount of a quaternary amine, (2) a polyolefin containing a particulate conductive filler, or (3) a mixture of (1) and (2).

The present invention also provides an antistatically conductive film suitable for masking during electrostatic spray painting.

DETAILED DESCRIPTION OF THE INVENTION

The acid copolymer is a polymer containing carboxylic acid moieties. By "polymers containing carboxylic acid moieties" as that term is used herein it is intended to mean copolymers of (i) a major amount by mol % of an alpha-olefin having the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl and (ii) a minor amount by mol % of an alpha,beta-ethylenically unsaturated carboxylic acid. Preferably, the alpha,beta-ethylenically unsaturated carboxylic acid is present in an amount by mol % of about 40% or less, more preferably about 30% or less, most preferably about 20% or less. Also, by the term "polymers containing carboxylic acid moities" it is intended to mean that the copolymer of an alpha-olefin having the formula $RHC{=}CH_2$ wherein R is H or C_1 to C_8 alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid may be wholly or partially neutralized with a suitable cation such as zinc cation or sodium cation. Thus, the polymer containing carboxylic acid moities may be an ionomer.

The acid copolymer need not necessarily comprise a two component polymer. Thus, although the olefin content of the acid copolymer preferably is at least 50 mol percent, more than one olefin may be employed. Also, other copolymerizable monoethylenically unsaturated monomers may be employed in combination with the olefin and the carboxylic acid comonomer. It is intended also to include terpolymers. Accordingly, acid copolymers or terpolymers suitable for use in the present invention include, but are not limited to, ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ethylene/itaconic acid copolymers, ethylene/methyl hydrogen maleate copolymers, ethylene/maleic acid copolymers, ethylene/methyl hydrogen maleate/ethyl acrylate terpolymers, ethylene/methacrylic acid/vinyl acetate terpolymers, ethylene/acrylic acid/vinyl acetate terpolymers, ethylene/acrylic acid/vinyl alcohol terpolymers, ethylene/propylene/acrylic acid terpolymers, ethylene/styrene/acrylic acid terpolymers, ethylene/acrylic acid/methyl methacrylate terpolymers, ethylene/methacrylic acid/ethyl acrylate terpolymers, ethylene/itaconic acid/methyl methacrylate terpolymers, ethylene/methacrylic acid/acrylonitrile terpolymers, ethylene/fumaric acid/vinyl methyl ether terpolymers, ethylene/vinyl chloride/acrylic acid terpolymers, ethylene/vinylidene chloride/acrylic acid terpolymers, ethylene/vinyl flouride/methacrylic acid terpolymers, and ethylene/chlorotrifluroethylene/methacrylic acid terpolymers.

The copolymer of an alpha-olefin having the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl and an alpha,beta-ethylenically unsaturated carboxylic acid representatively may be produced by the free radical copolymerization of ethylene and a carboxylic acid comonomer therefor such as acrylic acid or methacrylic acid. Suitable such acid copolymers are the Primacor™ polymers, supplied by Dow Chemical Company, Midland, Mich. Primacor is produced by the copolymerization of ethylene and acrylic acid. Ethylene-acrylic acid copolymers are herein referred to as EAA copolymer. A very suitable Primacor polymer is Primacor 1410 or Primacor 5981. Other suitable such acid copolymers are sold under the trade-name Nucrel by du Pont; they are produced by the copolymerization of ethylene and methacrylic acid. Ethylene-methacrylic acid copolymers are herein referred to as EMAA copolymers. Ionomers are commercially available as Surlyn™ from the E. I. du Pont de Nemours Company of Wilmington, Del., and are described in detail in U.S. Pat. Nos. 3,355,319 and 3,845,163.

The amine is a quaternary amine of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+[X]^-$$

wherein

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C═O or NHC═O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, citrate, propionate, tartrate or carbonate. Preferably, the C_1 to C_8 alkyl phosphate is methyl phosphate or ethyl phosphate, the C_1 to C_8 alkyl sulfate is methyl sulfate or ethyl sulfate, and the C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate is methanesulfonate, butanesulfonate, benzenesulfonate, or C_1 to C_{18} alkyl benzenesulfonate.

By "quaternary amine" as that term is employed herein, it is intended to include quaternary ammonium compounds and/or quaternary ammonium salts.

Suitable quaternary amines (QA) may be chosen from, but are not limited to, the methyl chloride salts of ethoxylated fatty amines. Commercial one are available

from the Tomah Division (Milton, Wis.) of Exxon Chemical and are represented by the formula:

$$
\begin{array}{l}
\quad (CH_2CH_2O)_qH \\
\quad\ | \\
Z-N-CH_3{}^{+} \quad Cl^{-} \\
\quad\ | \\
\quad (CH_2CH_2O)_tH
\end{array}
$$

where Z is an alkyl or alkoxy radical, and q+t is the total number of moles of ethylene oxide in the chains. Examples of commercially available ones are as follows:

COMMERCIAL QUARTERNARY AMINES

QA Product Indentification Number	Z	q + t
Q-14-2	$C_{10}OC_3$	2
Q-14-5	$C_{10}OC_3$	5
Q-14-15	$C_{10}OC_3$	15
Q-17-2	$C_{13}OC_3$	2
Q-S-2	Soya	2
Q-S-5	Soya	5
Q-S-15	Soya	15
Q-18-2	C_{18}	2
Q-18-5	C_{18}	5
Q-18-8	C_{18}	8
Q-18-10	C_{18}	10
Q-18-15	C_{18}	15
Q-T-2	Tallow	2
Q-T-5	Tallow	5
Q-T-15	Tallow	15
Q-DT-3	"Tallow Diamine"	3

Other very suitable quaternary amines are the ethyl sulfate salts or methyl sulfate salts of alkoxylated fatty amines. Commercial ones are available under the tradename Emerstat 6660 from Emery Industries and it is believed from applicants' own chemical analysis that they are represented by the formula: $(A)(A')N[(CH_2CH_2O)_nH]_2{}^{+}\ A'OSO_3{}^{-}$ where A is C_8 to C_{20} alkyl, A' is ethyl and n is an integer from 1 to 4. Also suitable are methyl sulfate salts such as that sold under the tradename Cyastate by Cyanamid; it has the formula $C_{11}H_{23}CONHC_3H_6N(CH_3)_3{}^{+}CH_3OSO_3{}^{-}$. Also suitable are ethosulfate salts such as that sold under the trade-name Larostat 264A Anhydrous, which is a modified soyadimethyl ethylammonium ethosulfate.

Additional QA's may be prepared by reacting a tertiary amine (TA) and an acid or alkylating agent, as further described in the Examples below.

The polymer containing carboxylic acid moieties and the quarternary amine are combined by mixing with heat. Optionally, a polymer compatible therewith, such as a polyolefin, may be blended in the mixture. Any suitable mixing means may be employed such as a blender or a twin screw extruder. The heat should be from about 50° C. to 290° C., more preferably about 100° C. to 250° C., even more preferably about 100° C. to 200° C. Then the resultant may be formed into a film such as by heat pressing on a platen or by any of the various methods further discussed below. The film is permanently antistatic. It will dissipate an applied charge of ±5000 Vdc in less than about 3000 ms, more preferably less than 2000 ms, using the method described in Federal Test Method Standard 101c, Method 4046.1, even after a 24 hour water shower. This is unlike prior polymeric films containing an antistatic agent to give them antistatic characteristics, which characteristics can be washed out after a 24 hour water shower because the agents operate by migrating to the surface and attracting moisture. Furthermore, in some embodiments, the films survive 1 day, more preferably 3 days, even more preferably 5 days, and most preferably 12 days in a hot oven at approximately 70° C. and still exhibit this static decay time of less than about 3000 ms, more preferably less than about 2000 ms.

Based on the % weight amount of polymer containing carboxylic acid moieties, it is preferred that the quaternary amine be present in a weight % amount up to about 50%, more preferably up to about 30%, even more preferably up to about 20%. Based on the total composition weight, which optionally may contain polyolefin, preferably the quaternary amine is present in a weight % amount of about 0.001% to about 30%, more preferably about 0.01% to about 20%, and even more preferably about 2% to about 10%.

Many polymer resins are suitable polymers for blending with the new, acid copolymer/quaternary amine. Unless specifically set forth and defined or otherwise limited, the terms "polymer" or "polymer resin" as used herein generally include, but are not limited to, homopolymers, copolymers, such as, for example block, graft, random and alternating copolymers, terpolymers etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited the terms "polymer" or "polymer resin" shall include all possible structures of the material. These structures include, but are not limited to, isotactic, syndiotactic and random symmetries. Particularly suitable for blending are the polyolefins. The term "polyolefin" as used herein generally includes, but is not limited to, materials such as polyethylene (PE), polypropylene (PP), ethylene-vinyl acetate (EVA) and the like, the homopolymers, copolymers, terpolymers etc. thereof, and blends and modifications thereof. The term "polyolefin" shall include all possible structures thereof, which includes, but is not limited to, isotactic, syndiotactic and random symmetries.

According to Modern Plastics Encyclopedia, 1985–86, polyethylenes having densities ranging from about 0.900 g/cc to about 0.935 g/cc are called low density polyethylenes (LDPE), while those having densities from about 0.936 g/cc to about 0.940 g/cc are called medium density polyethylenes (MDPE), and those having densities from about 0.941 g/cc to about 0.965 g/cc and over are called high density polyethylenes (HDPE). The older, classic low density types of polyethylenes are usually polymerized at high pressures and temperatures whereas, the older, classic high density types are usually polymerized at relatively low temperatures and pressures. The term "linear low density polyethylene" (LLDPE) as used herein, for a type of polyolefin, refers to the newer copolymers of a major amount of ethylene with a minor amount of one or more comonomers selected from C_3 to C_{10} alpha olefins such as butene-1, pentene-1, hexene-1, 4-methyl-pentene-1, octene-1, etc. in which the molecules thereof comprise long chains with few side chains or branched structures achieved by low pressure polymerization. LLDPE has a density preferably in the range from about 0.911 g/cc to about 0.935 g/cc, and more preferably in the range of from about 0.912 g/cc to about 0.928 g/cc. Also, very low density linear low density polyethylenes (VLDPE) may be employed, and such have a density from about 0.910 g/cc to about 0.860 g/cc, or even lower.

The term "ethylene vinyl acetate copolymer" (EVA) as used herein, for a type of polyolefin refers to a copolymer formed from ethylene and vinyl acetate (VA)

monomers. The ethylene derived units in the copolymer are present in major amounts by weight and the VA derived units in the copolymer are present in minor amounts by weight. For film making purposes, preferably the VA content of the EVA is from about 3% to about 25%.

The term "polypropylene" (PP) as used herein for a type of polyolefin refers to polymers of propylene, and includes homopolymers, copolymers, such as for example block, graft, random, and alternating, copolymers, terpolymers etc. and blends and modifications thereof.

The term "ethylene/alkyl-acrylate copolymer" (EAlAcr) as used herein refers to a copolymer formed from ethylene and alkyl acrylate wherein the alkyl moiety has 1 to 8 carbon atoms and the ethylene derived units in the copolymer are present in major amounts by weight and the alkyl-acrylate derived units in the copolymer are present in minor amounts by weight. Thus, the term "ethylene/methyl acrylate copolymer" (EMA) as used herein refers to a copolymer formed from ethylene and methyl acrylate monomers. The term "ethylene/ethyl acrylate copolymer" (EEA) as used herein refers to a copolymer formed from ethylene and ethyl acrylate monomers. The term "ethylene/butyl acrylate copolymer" (EBA) as used herein refers to a copolymer formed from ethylene and butyl acrylate monomers. Many suitable EBA's are commercially available and these have a BA content from about 3% up to about 18% by weight. USI is a commercial supplier of Resin No. 4895, which is an EBA having about 3% by weight butyl acrylate and a melt index of about 3 and a melting point of about 106° to 110° C.

Blends of all families of polyolefins, such as blends of EVA, EAlAcr, PP, LDPE, MDPE, HDPE, VLDPE, and LLDPE, may also be advantageously employed.

Some of the films were tested for suitability as a masking during electrostatic spray painting. The films were tested with a Ransburg Sprayability meter after equilibration for 1 hour at 35±5% relative humidity. A reading of about 90 or above is indicative of suitability as a masking during electrostatic spray painting. Preferably, the reading is about 100 or above. Meters are supplied by Ransburg Corp., Indianapolis, Ind.

Measuring the antistatic property: The antistatic property is exhibited by the ability of the polymer containing the agent to promote static charge decay, i.e. to dissipate a static charge. The polymer alone will not dissipate a static charge, but the polymer containing the agent is able to dissipate 99% of an applied static charge of ±5000 volts direct current (Vdc) in a short amount of time, i.e. less than 3 seconds, more preferably less than 2 seconds (2000 milliseconds). Federal Test Method Standard 101c, Method 4046.1, "Electrostatic Properties of Materials" states a static decay time (SDT) of less than 2000 ms and thus it is preferred to have a material that complies with 101c. Decay meters for measuring the SDT are commercially available, such as the 406C static decay meter supplied by Electrotech Systems, Inc. Unless otherwise indicated in the Examples below, the films, prior to SDT testing, were equilibrated at less than about 15% relative humidity (RH) at about room temperature (RT) for about 24 hours.

Some of the films were tested for surface resistivity and volume resistivity according to ASTM D257. There is not necessarily a correlation between the surface or volume resistivity of a film and the SDT.

Also there is not necessarily a correlation between a resistivity measurement and a Ransburg meter value measurement or between a SDT measurement and a Ransburg meter value measurement. However, usually a film that has a surface resistivity of about 10^{12} ohms/square or less, more preferably 10^{10} ohms/square or less, at about 12.5% RH or that has a SDT of about 3000 ms or less, more preferably about 2000 ms or less, at about 12.5% RH will also have a Ransburg meter value of about 90 or above, more preferably about 100 or above at 35±5% RH.

Manufacture of Films: Typically, in the manufacture of films, a suitable polymer usually in the form of pellets or the like, is brought into a heated area where the polymer feed is melted and heated to its extrusion temperature and extruded as a tubular "blown bubble" through an annular die. Other methods, such as "slot die" extrusion wherein the resultant extrudate is in planar, as opposed to tubular, form are also well known. If heat shrinkable film is desired, then after extrusion, the film is typically cooled and then reheated and stretched, i.e. oriented by "tenter framing" or by inflating with a "trapped bubble", to impart the heat-shrinkable property to the film, as is further described below. If desired, high energy irridiation, typically via an electron beam, preferably takes place prior to the stretching for orienting the film. However, for the present invention, such irradiation is not necessary since a very suitable packaging film having permanent antistatic characteristics is obtained without irradiation. Below, first is described the general process for making and orienting film. Then irradiation is described.

More particularly, manufacturing of films may be accomplished as follows. For instance, the manufacture of shrink films may be generally accomplished by extrusion (single layer films) or coextrusion (multi-layer films) of thermoplastic resinous materials which have been heated to or above their flow or melting point from an extrusion or coextrusion die in, for example, either tubular or planar (sheet) form, followed by a post extrusion cooling. The stretching for orientation may be conducted at some point during the cool down and while the film is still hot and within its orientation temperature range followed by completing the cooling. Alternatively, after the post extrusion cooling, the relatively thick "tape" extrudate is then reheated to a temperature within its orientation temperature range and stretched to orient or align the crystallites and/or molecules of the material and then cooled. The orientation temperature range for a given material or materials will vary with the different resinous polymers and/or blends thereof which comprise the material. However, the orientation temperature range for a given thermoplastic material may generally be stated to be below the crystalline melting point of the material but above the second order transition temperature (sometimes referred to as the glass transition point) thereof. Within this temperature range, the material may be effectively oriented. The terms "orientation" or "oriented" are used herein to describe generally the process steps and resultant product characteristics obtained by stretching and immediately cooling a resinous thermoplastic polymeric material which has been heated to a temperature within its orientation temperature range so as to revise the intermolecular configuration of the material by physical alignment of the crystallites and/or molecules of the material to improve certain mechanical properties of the film such as, for example, shrink tension and orienta-

tion release stress. Both of these properties may be measured in accordance with ASTM D 2838-81. When the stretching force is applied in one direction monoaxial orientation results. When the stretching force is simultaneously applied in two directions biaxial orientation results. The term oriented is also herein used interchangeably with the term "heat-shrinkable" with these terms designating a material which has been stretched and set by cooling while substantially retaining its stretched dimensions. An oriented (i.e. heat-shrinkable) material will tend to return to its original unstretched (unextended) dimensions when heated to an appropriate elevated temperature.

An "oriented" or "heat-shrinkable" material is defined herein as a material which, when heated to an appropriate temperature above room temperature (for example 96° C.), will have a free shrink of about 5% or greater in at least one linear direction.

Returning to the basic process for manufacturing the film as discussed above, it can be seen that the film, once extruded (or coextruded if it is a multi-layer film) and initially cooled, is then reheated to within its orientation temperature range and oriented by stretching. The stretching to orient may be accomplished in many ways such as, for example, by "trapped bubble" techniques or "tenter framing". These processes are well known to those in the art and refer to orientation procedures whereby the material is stretched in the cross or transverse direction (TD) and/or in the longitudinal or machine direction (LD or MD). After being stretched, the film is quickly cooled while substantially retaining its stretched dimensions to cool the film rapidly and thus set or lock-in the oriented molecular configuration.

Of course, if a film having little or no orientation is desired, e.g. non-oriented or non-heat shrinkable film, the film may be formed from a non-orientable material or, if formed from an orientable material may be formed from a tube by using a "trapped bubble" technique commonly known as the "hot blown" technique. In forming a hot blown film, the tube is not cooled initially after extrusion or coextrusion but rather is first stretched by a hot blown bubble essentially immediately after extrusion while the tube is still at an elevated temperature above the orientation temperature range of the material. Thereafter, the film is cooled, by well-known methods. Those of skill in the art are well familiar with this process and the fact that the resulting film has substantially unoriented characteristics. Other methods for forming unoriented films are well known. Exemplary, is the method of cast extrusion or cast coextrusion which, likewise, is well known to those in the art.

Whichever film has been made (the non-oriented molecular configuration or the stretch-oriented "heat-shrinkable" molecular configuration), it may then be stored in rolls and utilized to package a wide variety of items. If the material was manufactured by "trapped bubble" techniques the material may still be in tubular form or it may have been slit and opened up to form a sheet of film material. In this regard, the product to be packaged may first be enclosed in the material by heat sealing the film to itself where necessary and appropriate to form a pouch or bag and then inserting the product therein. Alternatively, a sheet of the material may be utilized to overwrap the product, or the product may be vacuum skin packaged with the material. These packaging methods are all well known to those of skill in the art.

If the material is of the heat-shrinkable, i.e. "oriented", type, then after wrapping, the enclosed product may be subjected to elevated temperatures, for example, by passing the enclosed product through a hot air tunnel. This causes the enclosing heat shrinkable film to shrink around the product to produce a tight wrapping that closely conforms to the contour of the product. As stated above, the film sheet or tube may be formed into bags or pouches and thereafter utilized to package a product. In this case, if the film has been formed as a tube it may be preferable first to slit the tubular film to form a film sheet and thereafter form the sheet into bags or pouches. Such bag or pouch forming methods, likewise, are well known to those of skill in the art.

Alternative methods of producing films of this type are known to those in the art. One well-known alternative is the method of forming a multi-layer film by an extrusion coating rather than by an extrusion or coextrusion process as was discussed above. In extrusion coating a first tubular layer is extruded and thereafter an additional layer or layers is simultaneously or sequentially coated onto the outer surface of the first tubular layer or a successive layer.

The above general outline for manufacturing of films is not meant to be all inclusive since such processes are well known to those in the art. For example, see U.S. Pat. Nos. 4,274,900; 4,229,241; 4,194,039; 4,188,443; 4,048,428; 3,555,604; 3,741,253; 3,821,182 and 3,022,543. The disclosures of these patents are generally representative of such processes and are hereby incorporated by reference.

Many other process variations for forming films are well known to those in the art. For, example, conventional pressing, thermoforming or laminating techniques (including corona laminating) may be employed. For instance, multiple layers may be first coextruded with additional layers thereafter being laminated thereon, or two multi-layer tubes may be coextruded with one of the tubes thereafter being laminated onto the other.

If a heat shrinkable, i.e. "oriented", film is desired, after extrusion and cooling, then after irradiation (or without irradiation), the tube may then be heated to soften it, and then the softened tube is passed through pinch rolls and stretch oriented by the trapped blown bubble technique discussed above. The disclosures of U.S. Pat. Nos. 3,456,044 and 3,555,604 are generally representative of orientation by the "double bubble" method and are hereby incorporated by reference.

Irradiation, if desired, may be accomplished by the use of high energy electrons, ultra violet radiation, X-rays, gamma rays, beta particles etc. Preferably, electrons are employed up to about 20 megarads (Mr) dosage level. The irradiation source can be any electron beam generator operating in a range of about 150 kilovolts to about 6 megavolts with a power output capable of supplying the desired dosage. The voltage can be adjusted to appropriate levels which may be for example 1,000,000 or 2,000,000 or 3,000,000 or 6,000,000 or higher or lower. Many apparatus for irradiating films are known to those of skill in the art. The irradiation is usually carried out at a dosage between about 1 Mr (10 kilogrey) and about 20 Mr (200 kilogrey), with a preferred dosage range of about 2 Mr (20 kilogrey) to about 12 Mr (120 kilogrey). Irradiation can be carried out conveniently at room temperature, although higher and lower temperatures, for example, 0° C. to 60° C. may be employed.

It is also generally well known in the art that irradiation, such as by electron beam irradiation, of certain polymeric film materials generally results in a material having improved heat shrink properties, abuse resistance, structural integrity, tensile strength, puncture resistance, and/or delamination resistance. Such physical toughness improvements from irradiation, are discussed in U.S. Pat. No. 3,022,543 (1962) to Baird et al, U.S. Pat. No. 4,178,401 (1979) to Weinberg and U.S. Pat. No. 3,741,253 to Brax et al.

An outside polymeric layer of a film may include a small amount of about 10% by weight or less, more desirably about 7% by weight or less of an antiblock, to help alleviate any tackiness. A suitable antiblock is EPE 8160 supplied by Teknor Apex. However, for the use of the film as a masking for electrostatic spray painting no antiblock would be added as the tackiness is desirable. For instance, in the acid copolymer/quaternary amine embodiment of the film, acid copolymer is present in the film, and acid copolymers, especially those of low molecular weight, are inherently adhesive at room temperature, a "cold stick" property desired so that the masking will adhere to the surface not to be painted. If additional adhesion is desired, the side of the film to be in adhering contact with the surface not to be painted can be coated with a coating of adhesive polymer in any convenient manner such as by dip coating, spray coating, brushing, gravure coating and the like. While the adhesive polymer can be applied directly to the film, a more uniform coating is applied by applying the adhesive polymer as a solution in a volatile solvent. Suitable volatile solvents include the saturated and unsaturated hydrocarbon, such as heptane, cyclohexane, toluene and the like; the halogenated hydrocarbons, such as chlorobenzene, chloroform, methylene chloride, and the like; hydrocarbon alcohols and hydrocarbon alcohol ethers, such as ethylene glycol, propylene glycol, and the like, and water. The coating of the adhesive polymer whether applied alone or from a solvent, is dried after application. Drying can be accomplished at room temperature or at an elevated temperature. The adhesive polymer is generally applied as a solution containing from about 0.5 to about 10, preferably from about 3 to 10, weight percent of the polymer in a solvent. The adhesive polymer is applied to the film to achieve a thickness of from about 0.05 to about 5.0 mils thereon. For instance, an aqueous solution of a low molecular weight EAA such as that marketed under the trade-name Primacor 5981 can be sprayed onto the film giving it "cold stick". An additional suitable adhesive polymer is polyvinyl alcohol. If desired, a release liner or paper can be applied to protect the adhesive prior to use.

The following Examples are intended to illustrate the preferred embodiments of the invention and comparisons thereto. It is not intended to limit the invention thereby.

Unless indicated otherwise in the Examples, the testing for static decay time (SDT) was done after equilibration for 24 hours, at about room temperature (RT), at less than about 15% relative humidity (RH). Also it is noted that sometimes SDT testing was done to samples that had been subjected to abuse such as 1 to 12 days in a hot, about 160° F. (71° C.), oven or a 24-hour water shower. Where the oven is designated as "humid", a beaker of water had been kept in the oven with the film sample during testing to maintain a "humid" atmosphere; otherwise the oven was simply a "dry" or "ambient" oven, without any water beaker.

Testing for suitability as a masking during electrostatic spray painting was done with a Ransburg Sprayability meter. Such meters are marketed by the Ransburg Corp., Indianapolis, Ind. A film suitable for masking will exhibit a meter reading above 90, more preferably above 100. Prior to testing films were first equilibrated for 1 hour at 35±5% relative humidity.

Testing for surface resistivity or volume resistivity was as per ASTM D257.

MATERIALS EMPLOYED IN THE EXAMPLES

ANTIBLOCK	INGREDIENTS			SUPPLIER
EPE 8160	Polyethylene Containing Micron Sized Silica			Teknor Apex
LLDPE	MI*	DENSITY	COMONOMER	SUPPLIER
DOWLEX 2045.03	1.1	0.920	Octene	Dow Chemical
EVA	MI	% VA	COMONOMER	SUPPLIER
LD 318.92	2.0	9	Vinyl Acetate	Exxon
EAA	MI	% BY WEIGHT ACRYLIC ACID	% BY WEIGHT ETHYLENE	SUPPLIER
PRIMACOR 1410	1.5	9	91	Dow Chemical
PRIMACOR 5981	300	20	80	Dow Chemical
ZINC METHACRYLATE IONOMER OF EMAA	FORMULA			SUPPLIER
SURLYN 1650	Partially zinc neutralized ethylene methacrylic acid copolymer			du Pont
QA	FORMULA			SUPPLIER
Q-14-2	$[C_{10}H_{21}OC_3H_6N(C_2H_4OH)_2CH_3]^+Cl^-$			Tomah Div. of Exxon
Emerstat 6660	$[H(CH_2)_{8-20}](C_2H_5)N[(C_2H_4O)_{1-4}H]_2$ + $C_2H_5OSO_3^-$			Emery Industries
Cyastat	$C_{11}H_{23}CONHC_3H_6N(CH_3)_3^+CH_3OSO_3^-$			Cyanamid
Larostat 264A Anhydrous	Modified soyadimethyl ethylammonium ethosulfate			Jordan / PPG / Mazer
TA	FORMULA			SUPPLIER
Empigen AB	Lauryl dimethylamine			Albright & Wilson

-continued

MATERIALS EMPLOYED IN THE EXAMPLES		
Empigen AY	$H(CH_2)_{10-18}(OC_2H_4)_{1-5}N(CH_3)_2$	Albright & Wilson
E-14-2	$C_{10}H_{21}OC_3H_6N(C_2H_4OH)_2$	Tomah Div., Exxon
DMCA	N,N-dimethylcocoamine	Akzo Chemie
ACID OR ALKYLATING AGENT	**FORMULA**	**SUPPLIER**
MSA	Methanesulfonic Acid	Aldrich
DBSA	$H(CH_2)_{12-18}C_6H_4SO_3H$	Alfa/Morton Thiokol
DES	Diethyl Sulfate	Aldrich

*MI is melt index.

EXAMPLE I

LLDPE and EAA (Primacor 5981) were premixed in parts by weight and then blended therein with heating was a QA in parts by weight. The resultant mix of LLDPE+EAA+QA was then further blended in an amount of 33⅓% by wt. with EAA (Primacor 1410) in an amount of 66⅔% by wt. and that was hot blown into an extruded, tubular film. Films were about 1.5 to 2 mils (0.04 to 0.05 mm) thick. What was made is listed in Table IA.

TABLE IA

60 parts by wt LLDPE [Dowlex 2045.03] 15 parts by wt QA [Q-14-2] 30 parts by wt EAA [Primacor 5981]	33⅓% by wt mix of LLDPE + EAA + QA 66⅔% by wt EAA [Primacor 1410] 100% Resultant Film

Then, the following electrical measurements were taken on samples of film as reported in Table IB.

TABLE IB

SAMPLE			
A	Static Decay Time as is		180 ms
B	Static Decay Time after 24 hours water shower		992 ms
C	Static Decay Time after days in hot oven at 71° C.	3 days	783 ms
		5 days	1149 ms
		9 days	7340 ms
		12 days	14683 ms
D	Surface resistivity as is	2×10^{10}	ohms/square
E	Volume resistivity as is	8.7×10^{10}	ohm-cm
	after 24 hr. water shower	1.5×10^{12}	ohm-cm
	after 12 day dry oven	1.8×10^{14}	ohm-cm

The results show the film performed well as an antistatic film both in terms of static decay time and resistivity, and was resistant to abusive aging, except that it did not survive 12 days in a hot oven with a desirable SDT of about 3000 ms or less.

EXAMPLE II

Films were made as in Example I except that this time the QA was Emerstat 6660 supplied by Emery Industries. The resultant film that was made is as listed in Table IIA below.

TABLE IIA

60 parts by wt LLDPE [Dowlex 2045.03] 15 parts by wt QA [Emerstat 6660] 30 parts by wt EAA [Primacor 5981]	33⅓% by wt Mix of LLDPE + EAA + QA 66⅔% by wt EAA [Primacor 1410] 100% Resultant Film

Then, the following electrical measurements were taken on samples of film as reported in Table IIB.

TABLE IIB

SAMPLE			
A	Static Decay Time as is		209 ms
B	Static Decay Time after 24 hours water shower		539 ms
C	Static Decay Time after days in hot oven at 71° C.	3 days	78 ms
		5 days	97 ms
		9 days	361 ms
		12 days	195 ms
D	Surface resistivity as is	1.2×10^{11}	ohms/square
E	Volume resistivity as is	2.8×10^{11}	ohm-cm
	after 24 hr. water shower	2.2×10^{12}	ohm-cm
	after 12 day hot dry oven	1.3×10^{12}	ohm-cm

The results show the film performed well as an antistatic film both in terms of decay time and resistivity, and was resistant to abusive aging.

EXAMPLE III

By blending with heat using a Berstorff twin screw extruder, a premix of pellets was made. First, 60 parts by weight EVA [LD318.92] and 30 parts by weight EAA [Primacor 5981] were mixed, and then added thereto was 15 parts by wt. QA [Emerstat 6660]. The resultant EVA+EAA+QA was then further blended with more polymer, and hot blown, 5-layer, extruded, tubular film having a thickness of about 4 mil (0.102 mm) was made. The ingredients of each layer were as recited in Table IIIA and are in % by weight.

TABLE IIIA

OUTSIDE LAYER 1	INTERIOR LAYER 2	CORE LAYER 3	INTERIOR LAYER 4	OUTSIDE LAYER 5
95% EVA 5% Anti-block	66⅔% EVA 33⅓% Mix of EVA + EAA + QA	90% LLDPE 10% Mix of EVA + EAA + QA	66⅔% EVA 33⅓% Mix of EVA + EAA + QA	95% EVA 5% Anti-block

Then, the following electrical measurements were taken on samples of film as reported in Table IIIB.

TABLE IIIB

Abuse Treatment Noted or Film Tested As is	Ohms/square Surface Resistivity	Ohms-cm Volume Resistivity	Static Decay Time (ms) 1 Hr. Equilibration for the Film as is or after abuse treatment	24 Hr. Equilibration for the Film as is or after abuse treatment
As is	1.8×10^{13}	7.0×10^{13}	111	222
1 Hr. Shower	1.4×10^{14}	2.1×10^{14}	7	177
3 Hr. Shower	5.7×10^{14}	1.6×10^{14}	Less Than MMSDT*	115
24 Hr. Shower	6.4×10^{12}	4.4×10^{14}	Less Than MMSDT	102
24 Hr. Hot Humid Oven	1.6×10^{13}	2.5×10^{14}	183	328
Hot Dry Oven				
Day 1	NT**	NT	332	185
Day 2	NT	NT	272	178
Day 3	NT	NT	180	164
Day 4	NT	NT	287	Won't Accept Full Charge
Day 5	NT	NT	148	115
Day 6	NT	NT	164	348
Day 7	NT	NT	359	200
Day 8	NT	NT	NT	455
Day 9	NT	NT	400	97
Day 10	NT	NT	213	259
Day 11	NT	NT	247	93
Day 12	4.2×10^{13}	1.0×10^{16}	299	164

*MMSDT = minimum measurable static decay time
**NT = not tested

It is noted from Table IIIB that while the resistivity measurements bordered between antistatic and insulative (i.e. 10^{13} to 10^{16}), the static decay times were excellent, well under the preferred 2000 ms or less even after the hot oven abuse or the water shower abuse. As for the film sample that would not accept a full charge after day 4 of the hot dry oven, while it is not intended to be bound to any theory, it is believed this happened due to a mechanical difficulty in that the sample was placed in the test meter in a curved or bowed position instead of a flat, taut position, with respect to the sensing electrode. (It is also noted that 2 similar 5-layer films were made, the only difference being that core layer 3 contained only 5% of the premix of EVA+EAA+QA or contained no premix of EVA+EAA+QA. These similar films performed substantially the same, but for not accepting a full charge during the SDT test after 10 to 12 days in a hot dry oven. While it is not intended to be bound to any theory, it is believed this was also due to a mechanical difficulty in that samples were placed in the test meter in a bowed position).

EXAMPLE IV

Six tubes of a 5-layer film were made as in Example III, but containing the following amounts of ingredients for each layer as recited in Table IVA below:

TABLE IVA

Layer 1	Layer 2	Layer 3	layer 4	Layer 5
90% EVA 10% Anti-block	66⅔% EVA 33⅓% Mix of EVA + EAA + QA	90% LLDPE 10% Mix of EVA + EAA + QA	66⅔% EVA 33⅓% Mix of EVA + EAA + QA	90% EVA 10% Anti-block

Samples of the 6 tubes of the 5-layer film were tested for static decay time after 1 hour of equilibration and the results were as reported in Table IVB below:

TABLE IVB

SAMPLE OF FILM	SDT (ms)
Tube 1	14
Tube 2	43
Tube 3	9
Tube 4	23
Tube 5	31
Tube 6	18

As can be seen, excellent SDT's were obtained.

Next 3 sets of 4 samples each of the 6 tubes of 5-layer Film were subjected to a 24-hour water shower. Then, each set was equilibrated for 1 hour, 24 hours, and 48 hours, respectively and then checked for SDT. The results were as reported in Table IVC below:

TABLE IVC

Tube	Sample	SDT (ms) After 1 Hour Equilibration	After 24 Hours Equilibration	After 48 Hours Equilibration
1	1	Less Than MMSDT*	24	29
1	2	Less Than MMSDT	23	41
1	3	Less Than MMSDT	15	23
1	4	Less Than MMSDT	16	24
2	1	Less Than MMSDT	60	54
2	2	Less Than MMSDT	54	50
2	3	Less Than	71	66

TABLE IVC-continued

		SDT (ms)		
Tube	Sample	After 1 Hour Equilibration	After 24 Hours Equilibration	After 48 Hours Equilibration
		MMSDT		
2	4	Less Than MMSDT	70	71
3	1	Less Than MMSDT	18	16
3	2	Less Than MMSDT	17	20
3	3	Less Than MMSDT	13	20
3	4	Less Than MMSDT	11	18
4	1	Less Than MMSDT	76	78
4	2	Less Than MMSDT	38	32
4	3	Less Than MMSDT	53	60
4	4	Less Than MMSDT	84	85
5	1	Less Than MMSDT	69	65
5	2	Less Than MMSDT	84	76
5	3	Less Than MMSDT	32	30
5	4	Less Than MMSDT	33	34
6	1	Less Than MMSDT	106	108
6	2	Less Than MMSDT	114	136
6	3	Less Than MMSDT	64	92
6	4	Less Than MMSDT	152	161

*MMSDT = Minimum measurable static decay time

As can be seen, when film was left to equilibrate for 24 hours, which is as per the specifications of Federal Test Method 101c, then excellent SDT's were obtained. Also, the film retained excellent SDT's even after further equilibration. Thus, these films indeed survived the vigorous abuse of a 24 hour water shower.

EXAMPLE V

A monolayer film was extruded from the pellets of premix having the ingredients as recited in Table V-A below:

TABLE V-A

60 parts by wt LLDPE [Dowlex 2045.03]
15 parts by wt QA [Q-14-2]
30 parts by wt EAA [Primacor 5981]

EXAMPLE VI

Quaternary amine additives QA1–QA5 (below) were prepared by mixing the following TA's (tertiary amines) and acids or alkylating agents without solvent for the indicated time/temp.

TABLE VIA

QA	Formula	TA (gms)	Acid or Alkylating Agent (gms)	Time/ Temp.
QA1	$H(CH_2)_{12}N(CH_3)_2H^+$ $CH_3SO_3^-$	Empigen AB (8.8)	MSA (3.2)	10 min./ 60° C.
QA2	$H(CH_2)_{12}N(CH_3)_2C_2H_5^+$ $C_2H_5OSO_3^-$	Empigen AB (8.8)	DES (5.2)	16 hr./ 60° C.
QA3	$H(CH_2)_{10\text{-}18}(OC_2H_4)_{1\text{-}5}N(CH_3)_2H^+$ CH_3SO_{3-}	Empigen AY (14.4)	MSA (3.2)	10 min./ 60° C.
QA4	$C_{10}H_{21}OC_3H_6N(C_2H_4OH)_2H^+$ $CH_3SO_3^-$	E14-2 (12.4)	MSA (3.2)	10 min./ 60° C.
QA5	$C_{10}H_{21}OC_3H_6N(C_2H_4OH)_2H^+$ $H(CH_2)_{12\text{-}18}C_6H_4SO_3^-$	E14-2 (12.4)	DBSA (10.0)	10 min./ 60° C.

Several quaternary amines (QA, 3.6 parts by weight) were blended with Primacor 5981 ethylene-acrylic acid copolymer (7.1 parts by weight) and LD318.92 ethylene-vinyl acetate copolymer (89.3 parts by weight). The blending was carried out by kneading at 130°-150° C. for approximately 20 minutes in a Brabender Plasticorder ® mixer. Samples of the resultant materials were pressed at approximately 1,000 psi (70 kg/cm) between platens heated to 150° C. Monolayer films of about 3 inches (7.6 cm) by 5 inches (12.7 cm) by 0.005 inch (0.013 cm) were thus obtained. The SDT of each film was determined before and after a 24-hour water shower. The results are summarized below:

TABLE VIB

Sample	QA	SDT Before Shower (ms)	SDT After Shower (ms)
1	QA5	490	2450
2	QA4	40	1000
3	QA1	90	510
4	QA2	100	880

These results demonstrate that the performance of the films tested was slightly degraded by an extensive water shower, but still less than 3000 ms for Sample 1 and less than the preferred 2000 ms for Samples 2, 3, and 4.

Next, several quaternary amines (QA 5.0 parts by weight) were blended with Primacor 1410 ethylene-acrylic acid copolymer (23.7 parts by weight) and LD318.92 ethylene-vinyl acetate copolymer (71.3 parts by weight). The blending and subsequent film preparation and testing were carried out as described above for the samples reported in Table VIB. The results were as follows:

TABLE VIC

Sample	QA	SDT Before Shower (ms)	SDT After Shower (ms)
5	Cyastat LS	420	500
6	Larostat 264A	590	630
7	QA3	110	650
8	QA1	550	720
9	QA2	70	180

These results demonstrate that there was almost no loss of static decay performance after extensive water

washing, and all SDT's were less than the preferred 2000 ms.

To demonstrate further permanence of these materials, the same samples 5 through 9 from after the water shower were further aged for 12 days in an oven at 70° C. and ambient humidity, i.e. a "dry" oven as there was no water beaker. SDT, surface resistivity, and volume resistivity for the resulting films are given below:

TABLE VID

RESULTS AFTER WATER SHOWER AND 12-DAY AGING AT 70° C.

Sample	SDT (ms)	Surface Resistivity (ohms/square)	Volume Resistivity (ohms-cm)
5	1660	1.1×10^{13}	4.4×10^{12}
6	1790	4.0×10^{12}	1.3×10^{12}
7	330	3.8×10^{11}	7.7×10^{11}
8	790	4.7×10^{11}	9.1×10^{11}
9	120	3.8×10^{11}	1.1×10^{11}

The results demonstrate that films produced with 5% of a QA additive in an EAA/EVA resin show excellent static decay times, surface resistivities, and volume resistivities, and are highly permanent, i.e., insensitive to water washout of additive and 12-day aging at elevated temperature.

COMPARATIVE EXAMPLE VII

A comparative sample was run for comparison with Sample 5 as reported in Tables VIC and VID above to show the result of omitting the ethylene-acrylic acid copolymer from the formulation. Thus, Cyastat LS (5.0 parts by weight) and LD318.92 ethylene-vinyl acetate copolymer (95.0 parts by weight) were kneaded at 130°-150° C. in a Brabender Plasticorder ® mixer. Effective mixing of these ingredients was never obtained, even after 4 hours of kneading. Reduction of the additive content to 2.5 parts by weight did not solve the problem. This demonstrates that an acid copolymer containing carboxylic acid moieties (i.e. the ethylene-acrylic acid copolymer) plays a critical role in compatibilizing the polyolefin with the ionic additive.

Another comparative sample was run but this time for comparison with Sample 9 as reported in Tables VIC and VID above to show the result of omitting the ethylene-acrylic acid copolymer from the formulation. Thus, QA2 (1.5 parts by weight) and LD318.92 ethylene-vinyl acetate copolymer (98.5 parts by weight) were kneaded at 130°-150° C. in a Brabender Plasticorder ® mixer. Effective mixing of these ingredients was obtained, finally after 4 hours of kneading. Some of the resultant material was pressed at approximately 1000 psi (70 kg/cm²) between platens heated to 150° C. Monolayer film of about 3×5×0.005 inches (7.6×12.7×0.013 cm) was thus obtained. The SDT of each film was determined before and after a 24-hour water shower. The results are summarized below:

TABLE VII

SDT Before Shower (ms)	SDT After Shower (ms)
580	over 30000

Also, after the shower, the film held a charge of 10 kilovolts, which indicates the antistatic property was lost. This demonstrates that an acid copolymer containing carboxylic acid moieties (i.e. the ethylene-acrylic acid copolymer) plays a critical role in providing permanent antistatic characteristics, i.e. enabling the film still to have a SDT less than about 3000 ms, more preferably less than about 2000 ms, after a 24-hour water shower.

EXAMPLE VIII

Quaternary amine QA2 (as defined in Table VIA, 6.0 parts) was blended with partially zinc neutralized ethylene-methacrylic acid-zinc methacrylate ionomer (23.5 parts) and LD318.92 ethylene-vinyl acetate copolymer (70.5 parts). The blending and subsequent testing were carried out as described in Example VI. The results were as follows:

Before Water Shower:	
SDT (ms)	470
Surface Resistivity (ohms/square)	1.7×10^{12}
Volume Resistivity (ohm-cm)	2.5×10^{12}
After 24-Hour Water Shower:	
SDT (ms)	880
Surface Resistivity (ohms/square)	7.6×10^{12}
Volume Resistivity (ohm-cm)	3.6×10^{10}
After 24-Hour Water Shower Followed by 12-Day/70° C. Aging	
SDT (ms)	460
Surface Resistivity (ohms/square)	1.7×10^{12}
Volume Resistivity (ohm-cm)	2.5×10^{12}

These results demonstrate that the film showed excellent static decay time, surface and volume resistivity, and resistance to water washout of additive and aging at elevated temperature.

EXAMPLE IX

Quaternary amine QA1 (5.0 parts) was blended with partially zinc neutralized ethylene-methacrylic acid-zinc methacrylate ionomer (23.7 parts) and LD318.92 ethylene-vinyl acetate copolymer (71.3 parts). The blending and subsequent testing were carried out as described in Example VI. The results were as follows:

Before Water Shower:	
SDT (ms)	230
Surface Resistivity (ohms/square)	5.2×10^{11}
Volume Resistivity (ohm-cm)	1.4×10^{12}
After 24-Hour Water Shower:	
SDT (ms)	150
Surface Resistivity (ohms/square)	6.5×10^{11}
Volume Resistivity (ohm-cm)	1.1×10^{12}
After 24-Hour Water Shower Followed by 12-Day/70° C. Aging:	
SDT (ms)	80
Surface Resistivity (ohms/square)	5.9×10^{11}
Volume Resistivity (ohm-cm)	5.9×10^{12}

These results demonstrate that the film showed excellent static decay time, surface and volume resistivity, and resistance to water washout of additive and aging at elevated temperature.

EXAMPLE X

The films of Examples I-IX are tested for electrostatic spray paintability with a Ransburg Sprayability meter after equilibration for 1 hour at 35±5% RH. Each exhibits a Ransburg conductivity value of 90 or above. Thus these films are suitable for use as a masking material for electrostatic spray painting.

EXAMPLE XI

Quaternary amine QA6, N,N-dimethyl-N-ethyl-N-cocoammonium ethosulfate, was prepared as follows: 9.36 g of N,N-dimethylcocoamine was combined with 6.10 g of diethyl sulfate. After mixing at 80° C. for 2-3 minutes, a clear liquid was formed in an exothermic process. On cooling, a waxy solid (m.p. 65°-75° C.) resulted (QA6).

Quaternary amine QA6 (4.44 g) was blended with 10 g Dow Primacor 1410 (ethylene-acrylic acid copolymer, 9% AA, 1.5 melt index) and 30 g Exxon LD318.92 (ethylene-vinyl acetate copolymer, 9% VA, 2.0 melt index). Blending was carried out in a Brabender Plasticorder mixer at 130° C. for 30 minutes. A sample of the resultant material was pressed at approximately 1,000 psi (70 kg/cm^2) between platens heated to 150° C. A monolayer film of about 3 inches (7.6 cm) by 5 inches (12.7 cm) by 0.005 inch (0.013 cm) was thus obtained. This sample was tested for electrostatic spray paintability as follows:

The sample was placed in a humidity-controlled chamber (35±5% RH) for one hour, then tested with a Ransburg Sprayability meter (Ransburg Corp., Indianapolis, Ind.). A sprayability reading of 118 (sprayable) was obtained. A reading of greater than 90 is indicative of electrostatic spray paintability, and a reading of over 100 is preferable. Therefore, this film exhibited a preferred electrostatic spray paintability.

For correlation purposes, the surface resistivity of the sample was also tested by two methods: First, the sample was equilibrated at 12.5±0.5% RH for 48 hours and tested with a Keithley 6105 resistivity adapter (Keithley Instruments, Cleveland, Ohio) connected to a Keithley 247 high voltage supply and a Keithley 485 picoammeter. With an applied voltage of 100 volts, a surface resistivity of 9.96×10^9 ohms/square was obtained. Second, the sample was equilibrated at 35±5% RH for >2 hours and tested with a TREK model 150 resistivity meter (TREK, Inc., Medina, N.Y.). A surface resistivity of 9×10^7 ohms/square was obtained.

EXAMPLE XII

Quaternary amine QA6 (4.44 g) was blended with 10 g partially zinc neutralized ethylene-methacrylic acid-zinc methacrylate terpolymer and 30 g Exxon LD318.92 as described in Example XI.

When prepared and tested as described in Example XI, a film sample of this material gave the following results:

Ransburg Conductivity: 110 (sprayable)

Surface Resistivity after equilibration at 12.5±0.5% RH for 48 hrs.: 2.00×10^{10} ohms/square

Surface Resistivity after equilibration at 35±5% RH>2 hrs.: 2×10^8 ohms/square

EXAMPLE XII

A film is made from polypropylene loaded with carbon black particulate filler. The film is spray coated on one side thereof with adhesive. The film shows a Ransburg meter reading over 90 after equilibration at 35±5% RH for 1 hour and thus is suitable for use as a masking for electrostatic spray painting.

What we claim is:

1. An electrostatically spray painted surface, comprising a surface, part of the surface being unmasked and part of the surface being masked with an antistatically conductive film suitable for masking during electrostatic spray painting, said film comprising (1) a polymer containing carboxylic acid moieties and admixed in said polymer an antistatically effective amount of a quaternary amine, (2) a polyolefin containing admixed therein a particulate conductive filler, or (3) a mixture of (1) and (2), whereby the unmasked part of the surface is covered with paint and the film is covered with paint and the masked part of the surface is free of paint, with the film keeping the masked part of the surface free of paint.

2. The electrostatically spray painted surface of claim 1 wherein:

(A) the polymer containing carboxylic acid moieties is a copolymer of (i) a major amount by mol % of an alpha-olefin of the formula $RCH{=}CH_2$ wherein R is H or C_1 to C_8 alkyl, and (ii) a minor amount by mol % of an alpha, beta-ethylenically unsaturated carboxylic acid, and

(B) the quaternary amine is of the formula

$$[(R^1)(R^2)(R^3)(R^4)N]^+ [X]^-$$

wherein

R^1 is selected from H, aryl, or C_1 to C_{50} alkyl optionally having one or more non-contiguous C=O or NHC=O or —S— or —O— in the carbon chain, or the same as R^2;

each of R^2, R^3, and R^4 is the same or different and selected from H, C_1 to C_{18} alkyl optionally substituted with one or more OH or from $-(R^5-O)_a-H$ where a is an integer from 1 to 10 and R^5 is ethylene or propylene; and

X is an anion selected from chloride, bromide, iodide, nitrate, fluoborate, phosphate, C_1 to C_8 alkyl phosphate, sulfate, C_1 to C_8 alkyl sulfate, formate, C_1 to C_8 alkyl or C_6 to C_{24} alkaryl or aryl sulfonate, acetate, trifluoroacetate, citrate, propionate, tartrate or carbonate.

3. The electrostatically spray painted surface of claim 2 wherein the polymer containing carboxylic acid moieties is ethylene-acrylic acid or ethylene-methacrylic acid and the amine is of the formula wherein: R^1 is C_8 to C_{20} alkyl, $C_{10}OC_3$, $C_{13}OC_3$, soya or tallow; R^2 and R^3 are both CH_3 or C_2H_4OH, R^4 is methyl or ethyl, and X is chloride, methyl sulfate or ethyl sulfate.

4. The electrostatically spray painted surface of claim 1 wherein the polyolefin is selected from ethylene vinyl acetate, ethylene alkyl acrylate, polypropylene, low density polyethylene, medium density polyethylene, high density polyethylene, linear low density polyethylene, very low density linear polyethylene, or mixtures thereof.

5. The electrostatically spray painted surface of claim 1 wherein the particulate conductive filler is selected from carbon, tin, nickel, zinc, copper, iron, aluminum, metallized mica, or mixtures thereof.

6. The electrostatically spray painted surface of claim 1 wherein said film has been coated with adhesive.

7. The electrostatically spray painted surface of claim 1 wherein said film is oriented.

8. The electrostatically spray painted surface of claim 1 wherein at least one film layer has been irradiated at a dosage up to about 20 Mr (200 kilogrey).

9. The electrostatically spray painted surface of claim 1 wherein the polymer containing carboxylic acid moieties is an ionomer containing carboxylic acid moieties partially neutralized by a metal salt.

10. An electrostatically spray painted surface comprising a surface, part of the surface being unmasked and part of the surface being masked with a permanently antistatically conductive film suitable for masking during electrostatic spray painting comprising a film obtained from mixing with heat and forming into a film (A) ethylene-acrylic acid copolymer or ethylene-methacrylic acid copolymer and (B) a quaternary amine of the formula $[(R^1)(R^2)(R^3)(R^4)N]^+ [X]^-$ where R^1 is a C_4 to C_{30} straight or branched alkyl optionally including one or more ether linkages, each of R^2 and R^3 and R^4 is the same or different and selected from methyl or ethyl, and X is chloride, methyl sulfate, or ethyl sulfate, whereby the unmasked part of the surface is covered with paint and the film is covered with paint and the masked part of the surface is free of paint, with the film keeping the masked part of the surface free of paint.

11. The electrostatically spray painted surface of claim 10 wherein the film comprises one or more layers made of the acid copolymer/quaternary amine, which film will exhibit an electrostatic spray painting meter reading of about 90 or above.

* * * * *